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PROPERTIES OF THIN LAYERS OF CADMIUM SULFIDE

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EFFECT OF CRYSTALLINE STRUCTURE ON THE PHOTOELECTRIC
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ABSTRACT

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Results of a study of the photoelectric properties of polycrystalline layers of cadmium sulfide as a function of their method of preparation are given. From a comparison of these results of X-ray structural and electronographic analysis it is found that the spectral distribution of the photocurrent, the absolute and relative photosensitivities, and the relaxation time are highly dependent on the substrate temperature. These differences are associated with a change in the phase composition and the degree of imperfection of the polycrystalline layers of cadmium sulfide.

It has been found in a number of papers (Ref. 1, 2) that the optical /132* properties of thin films of cadmium sulfide may differ considerably depending on the technological conditions of their preparation. As X-ray structural and electronographic analyses have shown (Ref.3, 4), both the crystalline structure of the layers of cadmium sulfide and their electrical

*Note: Numbers in the margin indicate pagination in the original foreign text.

and optical properties are determined to a large degree by technological factors.

The most important technological factors are: the substrate temperature, the vacuum or medium where sublimation takes place, and also subsequent temperature treatment of the films. In the literature devoted to the investigation of the properties of thin CdS layers, it is usually pointed out that their electrical properties depend on the technology of preparation to a greater degree than do the optical properties (Ref. 5). At the same time, there is little available information in the literature concerning the effect of the method of preparing the layers on their photoelectric properties.

This article presents the results of a study of the photo-electric properties of polycrystalline layers of cadmium sulfide as a function of their method of preparation, compared with the data furnished by X-ray structural and electronographic analyses.

Samples for the study were prepared by means of thermal evaporation of spectroscopically pure cadmium sulfide powder in vacuum at the pressure 10^{-5} mm Hg. Glass and quartz were used as substrates. The temperature of the substrate was varied within the range 80-500°C.

Photocurrent spectra were measured at room temperature, using continuous light in an optical system with double monochromatisation and with automatic recording on the EPP-09 electronic potentiometer. When continuous, automatic recording is employed, the large inertia of the thin layers for small illumination intensities can introduce a significant error into the spectral distribution of the photocurrent. However, this error can be reduced to a minimum by using very slow spectral recording.

In our experiments, the speed with which a photocurrent spectrum was /133 recorded was selected according to the relaxation time of a particular

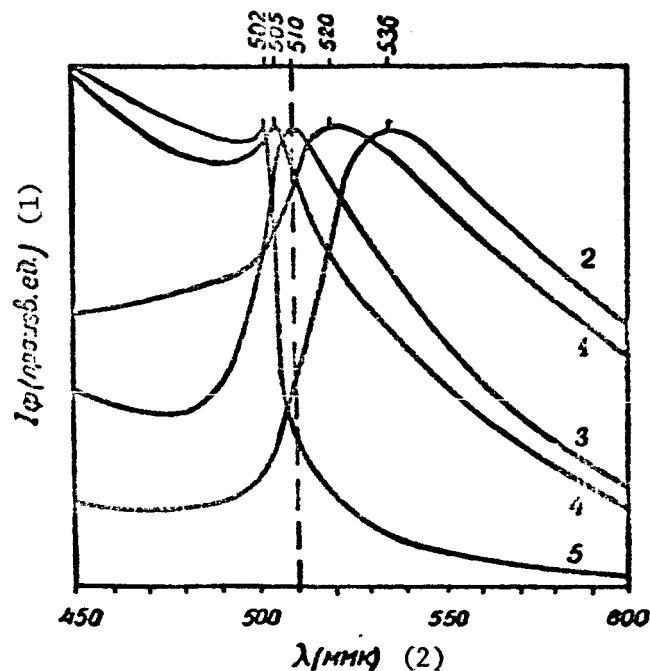


Figure 1

Photocurrent spectra of cadmium sulfide films, obtained at different substrate temperatures: 1-80°, 2-200°, 3-300° 4-400°, 5-500°C. Film thickness, 0.5-1.0 micron. 1- arbitrary unit; 2- millimicrons

sample, and amounted to 10A/min.

The data derived from measuring the spectral distribution of the photocurrent for samples obtained at different substrate temperatures are shown in Figure 1. The samples 1,2,3,4, and 5 were prepared at the substrate temperatures 80,200,300,400, and 500°C, respectively. The photocurrents of all the samples in Fig. 1 are normalized to their maximum. The curves shown in Figure 1 clearly illustrate the difference in photocurrent spectra for films with various substrate temperatures. When the substrate temperature increases, the photocurrent maximum is shifted to the short-wave part of the spectrum. For layers with the substrate temperature of 80°C (curve 1) the photocurrent maximum is located at 520 milli-microns, and the layers have high photosensitivity both for the wavelengths shorter than 510 millimicrons and for the longer ones (up to 1.2 millimicrons). For high-temperature samples (curves 4 and 5) practically the entire

sensitivity lies in the spectral region shorter than 510 millimicrons. Films prepared at 200°C, conversely, have their principal photosensitivity for wavelengths longer than 510 millimicrons, the photo-current maximum for such samples being located in the 520-550 millimicron region.

Since the samples are prepared under conditons guaranteeing freedom from extraneous admixtures, and since spectrally pure cadmium sulfide powder is used for sublimation, the differences in photoelectric properties of the films can be explained only by the influence of a disturbance in the stoichiometric compositon and a change in the crystalline structure of the substance. As has been established (Ref.3), thin layers of cadmium sulfide prepared at substrate temperatures ranging between 120-250°C are nonuniform in their phase compositon. In addition to the hexagonal /134 phase, they may contain up to 30% cubical phase, whereas at the substrate temperature outside of the interval in question (above 250°C and below 120°C) only hexagonal crystals are formed. Also, the hexagonal crystals growing on the substrate at a temperature below 120°C have an imperfect crystal lattice. Therefore, it can be assumed that the displacement of the photocurrent maximum in the direction of the long-wave region, from 505 to 520 millimicrons, is determined by the degree of imperfection of hexagonal crystals. Further long-wave displacement of the photosensitivity maximum is probably connected with the presence in the samples of a continually increasing percentage of cubical cadmium sulfide phase. For various samples with a substrate temperature of about 200°C, the spectral sensitivity maxima occur at wavelengths longer than 520 millimicrons. The longest wavelength positon of the photocurrent maximum which we succeeded in observing was 550 millimicrons. In such films the percentage of the

cubical phase, estimated from the relative density of reflexes on the electron-diffraction photograph, amounts to approximately 40%. We can assume that the principal photoelectric properties of such samples are determined by the cubical phase, and in this case it can be considered that the maximum of the spectral distribution of the photocurrent for a cubical modification of cadmium sulfide is located in the region of 550 millimicrons. This figure is in very good agreement with the data given by Bube (Ref. 6), who has measured photocurrent spectra for cubical cadmium sulfide.

The substrate temperature, at which the layer deposition takes place, exerts a great influence also on other characteristics of photo-conducting layers of cadmium sulfide. The relative photosensitivity (i.e. the ratio σ_1/σ_d of thin layers is increased with the rise in temperature, whereas the absolute photosensitivity is lowered. As the absolute photosensitivity of the samples increases, the inertia of photo-response increases also. Data on the relative photosensitivity and the relaxation-time of the photocurrent at the illumination intensity 10^3 lux for the samples from Figure 1 are presented in the table.

TABLE

$T, ^\circ\text{C}$	σ_{cb}/σ_t	τ sec
80	1,14	555
200	3,17	40
300	10,0	3,7
400	118	0,04
500	800	0,009

From the data obtained by electronographic analysis of cadmium sulfide layers, representing a mixture of cubical and hexagonal crystals, it is

known that the annealing of such films in the air within the temperature range 350–500°C leads to a considerable ordering of their structure in the direction of hexagonal CdS (Ref. 3). However, the cubical phase disappears completely only at temperatures higher than 500°C. Some data indicate the formation of an imperfect hexagonal structure during the transition from the cubical phase into the hexagonal one.

Obviously, these structural changes should manifest themselves in the spectral distribution of the photocurrent of the annealed samples.

Figure 2 presents the photocurrent spectra of cadmium sulfide films, obtained at the substrate temperature of 200°C, and representing a mixture of crystals of cubical (~ 25%) and hexagonal (~ 75%) forms. These layers were annealed in the air at temperatures of 400 and 500°C, respectively; the duration of annealing: 1 hour. The photocurrent curves are normalized /135 to their maxima. The photocurrent spectrum for a sample annealed at 400°C (curve 1, Fig. 2) practically coincides with the spectrum of the sample which was not annealed. The annealing of films at a temperature lower than 400°C does not lead to a change in the spectral distribution of the photocurrent, either. The displacement of the photocurrent maximum to the values characteristic of hexagonal cadmium sulfide takes place at an annealing temperature on the order of 500°C (curve 3, Fig. 2). Such a result can be fully explained, taking into account the results of the electro-nographic analysis.

The effect of annealing on the relative photosensitivity of the cadmium sulfide layers obtained at the substrate temperature 200°C is shown in Figure 3. As the annealing temperature increases, the conductivities of thin cadmium sulfide films, measured with light both present and

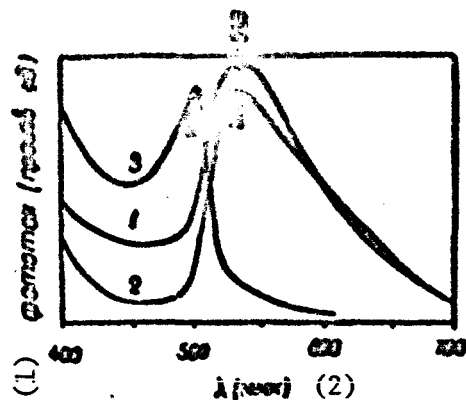


Figure 2

Photocurrent Spectra of Cadmium Sulfide Films Obtained at the Substrate Temperature 200°C (Curves 1 and 2). The Photocurrent Spectra of the Same Films, Annealed in the Air at the Temperature 400°C (Curve 1) and 500°C (Curve 3). Film Thickness 0.5-1.0 microns.
1- Photocurrent; 2- Millimicrons.

absent, decrease, whereas their ratio σ_1/σ_d is increased. The greatest changes are observed at temperatures about 500°C. A further increase in the annealing temperature, with the air present, leads to an intense formation on the surface of a sample of cadmium oxide which sharply increases the electric conductivity of the film, and leads to the disappearance of photosensitivity (dotted curve in Fig. 3).

The results of the influence of annealing, in an atmosphere of oxygen, on monocrystals and parched cadmium sulfide layers are described in (Ref. 7, 8). The usual result of annealing in oxygen consists of a decrease of the electric conductivity and in the appearance of additional photosensitivity in the region 600-700 millimicrons. In our case, conversely, annealing leads to a decrease in photosensitivity in a very broad spectral range (520-1000 millimicrons). These circumstances

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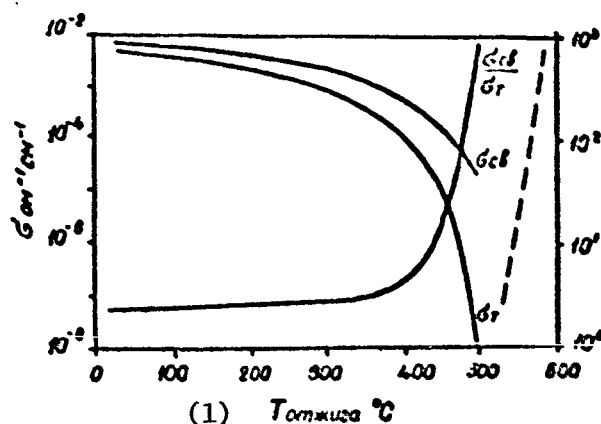


Figure 3

Change in Conductivity of Cadmium Sulfide Films with Light Present σ_l and with Light Absent σ_d as a Function of Air Annealing Temperature.

1- $T_{\text{annealing}}$

indicate that the primary influence on the properties of thin cadmium sulfide layers during annealing in an atmosphere of air is exerted by changing the phase composition and crystalline structure of the layer.

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